RAMAN SPECTRA OF ORGANIC CRYSTALS AT DIFFERENT LOW TEMPERATURES. II. ETHYL BENZENE AND BENZYL CHLORIDE.*

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Plate VI

ABSTRACT. The Raman spectra of crystals of ethyl benzene at −100°C and −180°C and of benzyl chloride at −50°C and −180°C have been investigated. Each of these substances in the solid state at a temperature a few degrees below the melting point yields four new Raman lines in the low-frequency region and this number increases to five when the solid is further cooled down to −180°C The intensity of some of the lines also increases with the lowering of temperature. It is pointed out that these results cannot be explained on the hypothesis that the lines are due to angular oscillation of the molecules pivoted in the lattice and that they can be explained by assuming that groups of associated molecules are formed in the solid state as pointed out earlier by Sirkar (1936).

The prominent Raman lines of the liquids are observed to become sharper with solidification of the liquid and some of the lines undergo slight changes in position. It is pointed out that these changes are also compatible with the formation of groups of associated molecules in the solid state.

INTRODUCTION.

To explain the origin of the low frequency Raman spectra observed in the case of differernt substances like benzene, naphthalene, diphenylether, para-dichlorobenzene, etc., in the solid state, Kastler and Rousset (1941), Bhagavantam (1941) and Rousset (1948) postulated that these lines are due to oscillations of the molecules pivoted in the crystal lattice. This hypothesis can be tested by studying the temperature-dependence of intensities and frequencies of the new lines as pointed out earlier by the author in the case of chlorobenzene and toluene (Ray 1950), benzene (Sirkar and Ray, 1950) and naphthalene (Ray, 1950). The results led to the conclusion that the low-frequency lines might be due to oscillations of the groups formed by association of the molecules and that the results could not be explained satisfactorily by the hypothesis put forward by Kastler and Rousset (1941) and Bhagvantam (1941). As the angular oscillations of the benzene ring pivoted in the lattice are expected to be greatly affected by the presence of substitution groups in the molecule, the results obtained in the case of a large number of substituted benzene compounds may be helpful in understanding the nature of oscilla-

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tions which give rise to these new lines in the case of the organic crystals It is therefore intended to study the Raman spectra of a few substituted benzene compounds in the solid state at different temperatures and the results obtained in the case of ethyl benzene and benzyl chloride are discussed in the present paper.

EXPERIMENTAL

The liquids ethyl benzene and benzyl chloride used for the present investigation were obtained from U. S. A. and were of chemically pure quality. The purity of the liquids was tested by comparing the Raman spectra of the liquids with those observed by the previous workers. In order to study the Raman spectra of the substances in the solid state at different low temperatures, the liquids distilled in vacuum were taken in cylindrical pyrex glass containers, each about one inch in diameter, provided with a long narrow neck with its mouth sealed. The container was suspended in a transparent Dewar vessel and the substance was kept at different temperatures by adjusting the position of the level of liquid oxygen in the transparent Dewar vessel. The temperature was measured with a pentane thermometer. Other experimental details were the same as those described by the author in a previous paper (Ray, 1950). Care was taken to solidify the liquid slowly in order to obtain a homogeneous mass so that the proportion of the extraneous light due to diffuse reflection from the volume of the crystal was small. The aperture of the collimator lens was effectively cut down in order to reduce the coma in the region of 4358 Å. In the case of ethyl benzene two spectrograms with the solid at about $-100°C$ and $-180°C$ were obtained and in the case of benzyl chloride the corresponding temperatures of the solid were about $-50°C$ and $-180°C$ respectively. Iron-arc spectrum was used as comparison in each case.

RESULTS

The spectrograms obtained for the two substances in the liquid state and in the solid state at different temperatures are reproduced in figures 1 and 2 in the Plate VI. The low-frequency region enlarged about six times is reproduced in figures 3 and 4. The frequency-shifts are given in Tables I and II in which those for the liquids reported by previous authors (Magat, 1934 and Petrikaln & Hochberg, 1929) are also included. No attempts were made to record the faint lines in the case of the liquids, as these lines were masked by the continuous background due to stray light in the case of the solid.

DISCUSSION OF RESULTS

(a) *New lines in the low-frequency region*

It can be seen from Tables I and II that in the case of both the compounds some new lines appear in the low-frequency region when the liquids

are solidified. The number of new lines in the case of solid ethyl benzene at −100°C (melting point −92.8°C) is four, the frequency-shifts being 45, 68, 95, 128 cm^{-1} respectively. When the temperature is lowered to −180°C the line at 68 cm^{-1} splits up into two lines at 63 and 81 cm^{-1} respectively. All the other three lines also shift a little away from the Rayleigh line with the lowering of temperature from −100°C to −180°C. In the case of benzyl chloride at −50°C (melting point −39°C) also four new lines appear in the low-frequency region at 46, 60, 86, 116 cm^{-1} respectively and of

TABLE I

Ethyl Benzene ($C_6H_5C_2H_5$)

Magat (1934) Liqiud $\Delta\nu$ in cm^{-1}	Present author		
	liquid at 30°C $\Delta\nu$ in cm^{-1}	Solid at about −100°C $\Delta\nu$ in cm^{-1}	Solid at about −180°C $\Delta\nu$ in cm^{-1}
	Continuous wing extending upto 100 cm^{-1}	45 (ob) ; e, k	48 (o) ; e, k
			63 (2) ; e, k
		68 (1b) ; e, k	
			81 (2) ; e, k
		95 (1) ; e, k	100 (2) ; e, k
		128 (o) ; e, k	130 (1) ; e, k
	145 (2b) ; e, k	148 (2) ; e, k	152 (2) ; e, k
457 (o)			
490 (1)	493 (1b) ; e, k	493 (1s) ; e, k ?	493 (1s) ; e, k
538 (o)	556 (1b) ; e		
620 (2)	623 (2) ; e, k	623 (2) ; e, k	620 (2) ; e, k
724 (o)	745 (1) ; e, k	745 (1) ; e, k	745 (1) ; e, k
773 (o)	772 4) ; e, k	768 (2) ; e, k	768 (2) ; e, k
	848 (1) ; e, k		
962	962 (2) ; e, k	962 (2) ; e, k	957 (1) ; e, k
1000 (4)	1000 (5) ; e, k	997 (4) ; e, k	994 (4) ; e, k
1032 (2)	1032 (3) ; e, k	1030 (2) ; e, k	1027 (2) ; e, k
1057 (o)	1055 (1) ; e, k	1052 (o) ; e, k	1050 (o) ; e, k
1106 (o)			
1156 (1)	1156 (2) ; e, k	1157 (1) ; e, k	1158 (1) ; e, k
1176 (1)	1175 (o) ; e, k	1170 (1) ; e, k	1170 (1) ; e, k
1204 (3,	1205 (3) ; e, k	1205 (2) ; e, k	1205 (2) ; e, k
1260 (1)	1262 (ob) ; e, k	1261 (1) ; e, k	1259 (1) ; e, k
	1325 (1b) ; k		
1381 (o)			
1448 (1dd)	1448 (1d) ; e, k	1448 (1) ; e, k	1450 (1) ; e, k
1465 (1dd)			
1587 (1)	1588 (1) ; e, k	1586 (1) ; e, k	1586 (1) ; e, k
1608 (3)	1608 (4) ; e, k	1608 (2) ; e, k	1604 (2) ; e, k
	2880 (1b) ; e, k	2878 (1b) ; e, k	2860 (1b) ; e, k
	2912 (1) ; e, k	2912 (ob) ; e, k	
2936 (2d)	2936 (2) ; e, k	2930 (2) ; e, k	2925 (o) ; k
			2942 (2) ; k
			2957 (1) ; k
	3036 (1) ; e, k	3040 (1) ; k	3036 (2) ; k
3053 (2)		3050 (4) ; k	3050 (4) ; k
3066 (2)	3064 (5b) ; e, k	3068 (1) ; k	3060 (o) ; k

these the line at 86 cm^{-1} splits up into two lines at 82 and 88 cm^{-1} respectively at −180°C. The centre of gravity of these two lines is at 85 cm^{-1} and therefore, the line does not shift appreciably with the lowering of temperature of the solid. Of the remaining three lines the line at 46 cm^{-1} remains in the same position and the lines 86 and 116 cm^{-1} shift respectively to 88 and 119 cm^{-1} when the crystal is cooled from −50°C to −180°C. Thus it can be concluded that these changes in position of the lines in the low-frequency region in this case are smaller than and quite different from those observed in the case of ethyl benzene.

An attempt may now be made to explain these results on the different hypotheses put forward by previous workers to explain the origin of these new lines in the low-frequency region. According to the theory put forward by Kastler and Rousset (1941) and also by Bhagavantam (1941) the lines are due to angular oscillations of the rigid molecule pivoted in the lattice, and the frequencies of such oscillations depend on the moments of inertia of the molecule about three axes. The line with minimum frequency-shift is due to the oscillation of the pivoted molecule about an axis perpendicular to the plane of the molecule, according to the theory mentioned above. The

TABLE II

Benzyl Chloride $C_6H_5CH_2Cl$

Petrikaln & Hochberg (1929) liquid $\Delta\nu$ in cm^{-1}	Present author		
	Liquid at 25°C $\Delta\nu$ in cm^{-1}	Solid at about −50°C $\Delta\nu$ in cm^{-1}	Solid at about −180°C $\Delta\nu$ in cm^{-1}
	Continuous wing extending upto 100 cm^{-1}	46 (1); e, k 60 (1); e, k	46 (2); e, k 62 (2); e, k 82 (3); e, k
		86 (2); e, k	88 (3); e, k
		116 (2); e, k	119 (3); e, k
138	134 (4b); e, k	136 (5); e, k	142 (5s); e, k
275	274 (ob); e, k		
338			
476	478 (1b); e	478 (1b); e	478 (2); e k
622	625 (2); e, k	625 (2); e, k	625 (3); e, k
682	681 (3b); e, k	673 (4b); e, k	670 (5s); e, k 674 (1s); e
772	767 (2); e, k	767 (2); e, k	767 (3s); e, k
816	820 (1); e, k		
1001	997 (10); e, k	997 (11); e, k	997 (12); e, k
1038	1025 (1); e, k	1025 (1); e, k	1025 (1); e, k
1156	1162 (1); e, k	1162 (1); e, k	1163 (2); e, k
1212	1210 (2); e, k	1212 (2); e, k	1210 (2); e, k
1267	1263 (1b); e, k	1265 (4); e, k	1265 (4s); e, k
1608	1608 (5); e, k	1608 (5); e, k	1608 (6); e, k
2967	2967 (2b); k	2975 (1); k	2975 (1); k
3064	3063 (3); k	3065 (3); k	3060 (3); k

Fig. 1

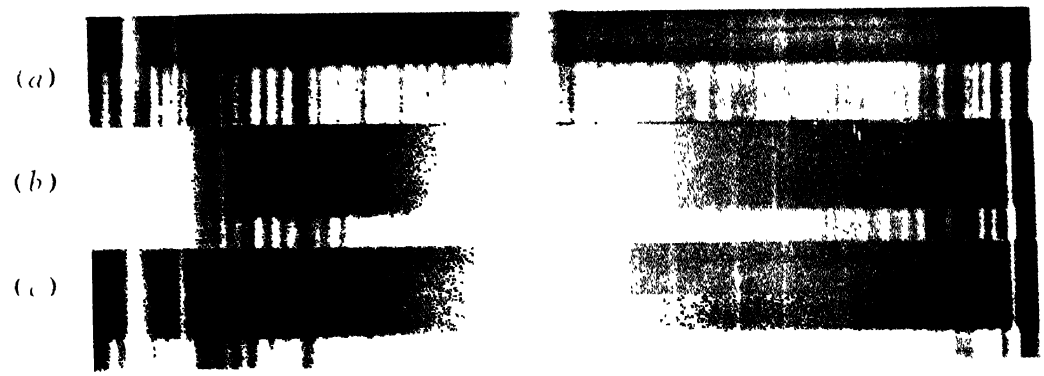

Fig. 2

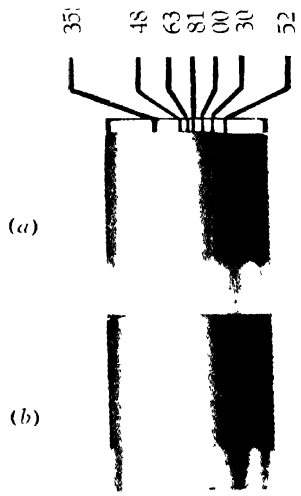

Fig. 3.

(a) $C_6H_5C_2H_5$—Liquid at 30°C
(b) ,, —Solid at about − 100°C
(c) ,, − Solid at about —180°C
(a) $C_6H_5C_2H_5$ —Solid at about —180°C
(b) ,, —Solid at about —100°C

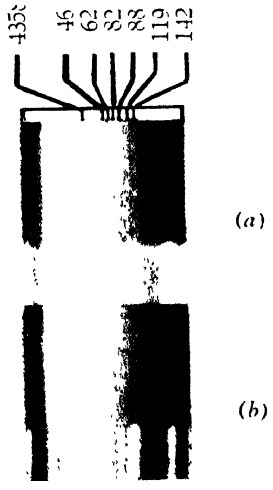

Fig. 4.

Fig 2 (a) $C_6H_5CH_2Cl$ - Liquid at 25°C
(b) ,, —Solid at about − 50°C
(c) ,, —Solid at about − 180°C
Fig 4. (a) $C_6H_5CH_2Cl$—Solid at about —180°C
(b) ,, —Solid at about − 50°C

examination of the data compiled in Table III, however, shows that molecules having widely different moments of inertia yield a line having the same minimum frequency-shift. For instance, the line at about 47 cm^{-1} is present in the Raman spectra of benzene, chlorobenzene, toluene, benzyl chloride and ethyl benzene at −180°C.

TABLE III

Substance in the solid state	temperature	$\Delta\nu$ in cm^{-1}
Benzene	−180°C	47, 53, 78, 95, 134
chloro benzene	−180°C	46, 63, 83, 102, 135
Toluene	−180°C	47, 66, 86, 108, 127
Benzyl Chloride	−180°C	46, 62, 82, 88, 119
Ethyl benzene	−180°C	48, 63, 81, 100, 130

Careful examination of the direct mercury arc spectrum photographed with the same spectrograph has shown that there is no trace of any line in this position and therefore this line is not a spurious one. The presence of this line in all these cases thus clearly shows that the frequency of the line is not at all determined by the moment of inertia of the molecule, because the moment of inertia of the benzene molecule about an axis perpendicular to its plane is much smaller than that of any of the other four compounds mentioned in Table III. Such a conclusion is further supported by the fact that corresponding to a line at 134 cm^{-1} in the case of benzene, chlorobenzene yields a line at 135 cm^{-1}, although the corresponding moment of inertia of chlorobenzene is much larger. Thus these results do not support the hypotheses that the lines are due to angular oscillations of the molecules pivoted in the lattice. The increase in intensity of some of the lines with the lowering of temperature also cannot be explained on such a hypothesis.

The results can, however, be explained on the hypothesis put forward by Sirkar (1936) that these lines are due to inter-molecular oscillations in groups of associated molecules. It is well known that a particular atomic group, present in different molecules, yields Raman lines of almost identical frequencies in all the cases, and therefore, it could be expected that the benzene ring present in the different molecules mentioned in Table III would yield almost the same set of lines due to intermolecular oscillations in associated groups of molecules. The results given in Table III corroborate such a statement, because each of these substances, having widely different molecules, yields five lines.

The frequency of the line at 53 cm^{-1} increases to about 63 cm^{-1} on substituting one of the hydrogen atoms by a chlorine atom, a CH_2Cl group

or a CH_3 group. This increase may be due to the fact that the strength of the virtual bond between two associated molecules is larger in the case of the substituted molecules which are polar than that in the case of the benzene molecule. On the other hand, frequency of this line would diminish considerably with the substitution of the hydrogen atom in the benzene molecule had the line been due to the angular oscillation of the molecule about an axis in the plane of the molecule.

(*b*) *Molecular frequencies*

As regards the frequency-shifts of the lines due to intramolecular oscillations the changes, observed with the solidification and with further lowering of the temperature of the solid up to about −180°C, are larger in the case of ethylbenzene than those observed in the case of benzyl chloride. Thus in the former case the frequency-shifts of the lines 145, 772, 1000, 1032, 1055, 1175, 2936 and 3036 cm^{-1} change respectively to 148, 768, 997, 1030, 1052, 1170, 2930 and 3040 cm^{-1} and the line 3064 cm^{-1} splits up into two lines at 3050 and 3068 cm^{-1} when the liquid is solidified, while in the latter case only the lines 134, 681 and 2967 cm^{-1} undergo changes in position with the solidification of the liquid. On further cooling the solid to a temperature of −180°C, the lines 148, 623, 962, 997, 1030, 1052, 2878, 3040 and 3068 cm^{-1} of solid ethyl benzene shift to 152, 620, 957, 994, 1027, 1050, 2860, 3036 and 3060 cm^{-1} respectively and the line 2930 cm^{-1} splits up into three lines at 2925, 2942 and 2957 cm^{-1} respectively. As the line 2878 cm^{-1} is due to the C-H oscillation in the C_2H_5 group, it is evident that strength of the C-H bond changes considerably with the lowering of temperature of the solid. In the case of benzyl chloride, on the other hand, very little change takes place in the positions of lines with the lowering of temperature of the solid except in the case of the lines 136, 673 and 3065 cm^{-1} which shift respectively to 142, 670 and 3060 cm^{-1}. Further, the line 670 cm^{-1} is accompanied by a weak satellite at 674 cm^{-1} at −180°C.

These data thus show that the changes taking place in the strength of the bonds are different for the two molecules and that the modes of oscillations, the frequencies of which are affected by the change of temperature, are not identical in the two cases. This may be due to the fact that the modes of oscillations which are affected by association of the molecules depend on the actual location of the point at which the molecule is associated with its neighbour.

Examinations of the spectrograms reproduced in Plate VI shows that the prominent Raman lines due to single molecules observed in the case of each of the two liquids become much sharper when the liquid is solidified. As pointed out in previous papers (Ray, 1950; Sirkar & Ray, 1950), these results are contradictory to the hypothesis put forward by Bhagavantam (1941) that it is the change of polarisability of the unit cell containing more than one molecule which determines the intensity of the Raman line. If such

hypothesis would be correct each of the prominent Raman lines would be split up into two components, one polarised and another totally depolarised in each case. Since no such doubling is observed even at −180°C this probability of the occurrence of coincidence or opposition of phases of oscillation of the molecules in the unit cell is negligible in comparison with that for the random oscillation of the single molecules, and the Raman lines are due to changes of polarisability in the single molecule in the crystal.

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REFERENCES

Bhagavantam, S. 1941, *Proc. Ind. Acad. Sc.*, **13A**, 543.
Kastler, A and Rousset A., 1941, *Comptes Rendus*, **212**, 645.
Magat, M., 1934, *Annual Tables, Paris*, **26**, 73.
Petrikaln, A., and Hochberg, J., 1929, *Zeit. f. Phys. Chem.*, **1**, 299.
Rousset, A., 1948, *Jour de. Phys.*, **9**, 101.
Ray, A. K., 1950, *Ind. Jour. Phys.*, **24**, 111.
Ray, A. K., 1950, *Ibid.*, **24**, 539.
Sirkar, S. C., 1936, *Ibid.*, **10**, 109, 189.
Sirkar, S. C., and Ray, A. K., 1950, *Ibid.*, **24**, 189.